Rotational resolved pulsed field ionization photoelectron spectroscopy study of $O_2^+(a^4\Pi_u\ v^+=0\text{-}18)$ and $O_2^+(A^2\Pi_u, v^+=0\text{-}12)$

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INTRODUCTION

We have obtained rotationally resolved pulsed field ionization photoelectron (PFI-PE) spectra for O_2 in the energy range of 16.00-18.13 eV, covering the ionization transitions $O_2^+(a^4\Pi_u, v^+=0\text{-}18, J^+) \leftarrow O_2(X^3\Sigma_g^-.\ v''=0, N'')$ and $O_2^+(A^2\Pi_u, v^+=0\text{-}12, N^+) \leftarrow O_2\ (X^3\Sigma_g^-.\ v''=0, N'')$. Although these $O_2^+(a^4\Pi u$ and $A^2\Pi_u, v^+)$ PFI-PE bands have significant overlaps with each other and $O_2^+(X^2\Pi_g)$, we have identified all the $O_2^+(a^4\Pi_u,\ v^+=0\text{-}18)$ and $O_2^+(A^2\Pi_u,\ v^+=0\text{-}12)$ bands by simulation of spectra obtained using supersonically cooled O_2 samples with rotational temperatures ≈20 and 220 K. While these $v^+=4\text{-}18$ and $v^+=0\text{-}12$ PFI-PE bands represent the first rotationally resolved photoelectron data for $O_2^+(a^4\Pi_u)$ and $O_2^+(A^2\Pi_u)$ respectively, the PFI-PE bands for $O_2^+(a^4\Pi_u, v^+=10\text{-}18)$ and $O_2^+(A^2\Pi_u, v^+=9$ and 10) are the first rotationally resolved spectroscopic data for these levels. The simulation also allows the determination of accurate ionization energies, vibrational constants, and rotational constants for $O_2^+(a^2\Pi_u, v^+=0\text{-}18)$ and $O_2^+(A^2\Pi_u, v^+=0\text{-}12)$. The observed intensities of spin-orbit components for the majority of vibrational bands for $O_2^+(a^2\Pi_u, v^+)$ are in accordance with the forced spin-orbit/rotational autoionization mechanism. The analysis of the PFI-PE spectra supports the conclusion of the previous emission study that the $O_2^+(A^2\Pi_u, v^+=9$ and 10) states are strongly perturbed by a nearby electronic state.

EXPERIMENT

The beamline consists of a 10 cm period undulator, a gas harmonic filter, a 6.65m off-plane Eagle monochromator, and a photoion-photoelectron apparatus, all of which has been discussed in detail previously. In the present experiment, Ne and He are used in the harmonic gas filter, where higher undulator harmonics with photon energies greater than 21.56 and 24.59 eV are suppressed respectively. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by either a 2400 lines/mm (dispersion = 0.32 Å/mm) or a 4800 lines/mm grating (dispersion = 0.32 Å/mm) before entering the experimental apparatus.

The ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns. Each electron bucket emits a light pulse of 50 ps with a time separation of 2 ns between successive bunches. In each storage ring periods, a dark gap (16~112 ns) consisting of 8~56 consecutive unfilled buckets exists for the ejection of cations from the orbit.

A continuous molecular beam of pure O_2 was produced by supersonic expansion through a stainless steel nozzle (diameter = 0.127 mm) at a stagnation pressure of 760 Torr and a nozzle temperature of 298 K. The molecular beam was skimmed by a circular skimmer (diameter = 1 mm) before intersecting the monochromatized VUV light beam 7 cm downstream in the photoionization region. As shown below, the simulation of PFI-PE spectra suggests that the rotational temperature for O_2 achieved is ≈220 K in this experiment.

The $O_2^+(a^4\Pi_u, v^+=0, 2,$ and 6-11) and $O_2^+(A^2\Pi_u, v^+=0\text{-}3$ and 5) PFI-PE bands were re-examined in another experiment performed about three years later using a colder O_2 molecular

beam sample with a rotational temperature of ≈20 K. A new synchrotron-based PFI-PE detection scheme, which relies on the time-of-flight (TOF) selection of PFI-PEs, is used in the recent study. The absolute photon energy scale was calibrated using the $Ar^+(^2P_{3/2})$, and $Ne^+(^2P_{3/2})$ PFI-PE bands recorded under the same experimental conditions before and after each scan. This calibration procedure assumes that the Stark shift for ionization thresholds of target gases and the rare gases are identical. On the basis of previous experiments, the accuracy of the energy calibration is believed to be within ±0.5 meV.

RESULTS AND DISCUSSION

The main electronic configuration for the $O_2(X^3\Sigma_g^-)$ ground state is $KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$. The ejection of an electron from a $1\pi_u$ bonding orbital results in the $O_2^+(a^4\Pi_u)$ and $O_2^+(A^2\Pi_u)$ excited states. Both these excited states, together with the ground $O_2^+(X^2\Pi_g)$ state, converge to the first dissociation limit $O(^3P) + O^+(^4S_0)$, but with significantly shallower potential wells than that of the $O_2^+(X^2\Pi_g)$ state.

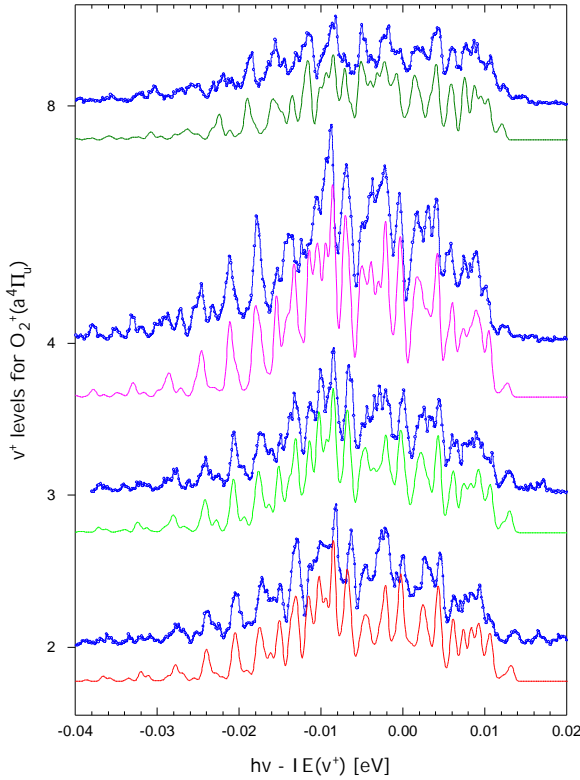

Figure 1. Simulated and experimental PFI-PE spectra for $O_2^+(a^4\Pi_u, v^+=2\text{-}4$ and 8) obtained using a 220 K O_2 sample. The horizontal scale is hν - IE(v⁺), where hν is the photon energy. For each v⁺ state, the upper spectrum (open circles) is the experimental spectrum, while the simulated spectrum (solid curve) is shown underneath the experimental curve. The simulated spectrum for v⁺=8 has included contributions from the PFI-PE bands for $O_2^+(a^4\Pi_u, v^+=8)$ and $O_2^+(A^2\Pi_u, v^+=0)$.
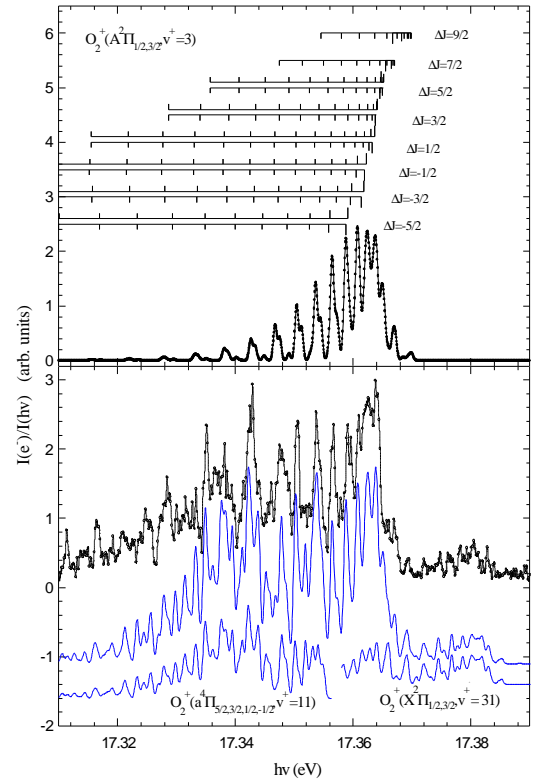
Figure 2. Deconvolution of the PFI-PE bands for $O_2^+(A^2\Pi_{1/2,3/2u}, v^+=3)$ from the corresponding mixed bands by BOS simulation. (upper panel): The deconvoluted PFI-PE bands for $O_2^+(A^2\Pi_{1/2,3/2u}, v^+=3)$. The rotational transitions to the $O_2^+(A^2\Pi_{1/2u}, v^+, N^+)$ and $O_2^+(A^2\Pi_{3/2u}, v^+, N^+)$ from $O_2 (X^3\Sigma_g^-, v''=0, N'')$ are marked using downward pointing and upward pointing stick marks, respectively. The ΔJ rotational branches are also marked. (Lower panels): The top spectra (open circles) are the mixed experimental PFI-PE spectra obtained using an O_2 sample with a rotational temperature of ≈220 K. The deconvoluted PFI-PE bands (solid lines) for $O_2^+(a^4\Pi_u, v^+=11)$ and $O_2^+(X^2\Pi_{1/2,3/2g}, v^+=31)$ are shown as the bottom spectra. The middle spectra (solid lines) represent the sums of the deconvoluted band.

A. Spectral simulation and assignment of rotational branches

The relative intensities for rotational structures resolved in individual vibrational PFI-PE bands for $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u}$, v^+=0-18) $O_2^+(A^2\Pi_u$, v^+=0-12) were simulated using the Buckingham-Orr–Sichel (BOS) model, which was derived to predict rotational line strength observed in single-photon ionization of diatomic molecules. This procedure has been described in detail previously. The BOS model is a one-electron model and does not take into account any channel interactions. Both ionization transitions, $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u}) \leftarrow O_2(X^3\Sigma_g^-)$ and $O_2^+(A^2\Pi_{1/2,3/2u}) \leftarrow O_2(X^3\Sigma_g^-)$ can be classified as a Hund's case (b) to (a) transition and is similar to the $O_2^+(X^2\Pi_{1/2,3/2g}) \leftarrow O_2(X^3\Sigma_g^-)$ system. For both states, we obtained excellent simulation curves for most of the experimental data. Figure 1 shows the rotationally resolved PFI-PE bands for $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u}$, v^+=2, 3, 4, 8) $\leftarrow$ $O_2(X^3\Sigma_g^-$, v"=0) together with their simulations as a function of hv-IE. Figure 2 depicts the deconvoluted spectrum of $O_2^+(A^2\Pi_{1/2,3/2u}$, v^+=3) from $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u}$, v^+=11) and $O_2^+(X^2\Pi_g$, v^+=31) together with rotational transition assignments.

B. Photoionization mechanism

For $O_2^+(A^2\Pi_u)$, we consistently observed a mismatch between the position of the band maximum observed in the experimental spectrum and that in the simulated spectra. The intense, sharp peak at 17.462 eV resolved in the v^+=4 band is consistent with a local enhancement by the near-resonant autoionization mechanism. The structure observed for the v^+=10 band is likely to result from a different mechanism. Near v^+=9 and 10, a possible candidate for a perturbative state is suggested to be $^2\Sigma_u^+$ state, which was predicted in *ab intio* configuration interaction calculations. In this experiment, the special sets of BOS coefficients needed for the simulation of the $O_2^+(A^2\Pi_u$, v^+=9 and 10) bands can be taken as support that these states are strongly perturbed.

For $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u})$, v^+=1~9, we find that the intensities for the spin-orbit components are in the order $F_1(a^4\Pi_{5/2}) \geq F_2(a^4\Pi_{3/2}) > F_3(a^4\Pi_{-1/2}) > F_4(a^4\Pi_{-1/2})$. The intensity of the highest energy spin-orbit component $F_4(a^4\Pi_{-1/2})$ for v^+=11, 12, 15, and 16 are also found to be lowest. This observation is in accord with that found in the PFI-PE bands for $O_2^+(a^4\Pi_{5/2,3/2,1/2,-1/2u}$, v^+=1 and 2) recorded in the previous VUV laser study. The observed intensities distributions for the spin-orbit components were attributed to the forced spin-orbit/rotational autoionization mechanism. This forced autoionization mechanism is field induced and strongly depends on the field strength. Our observation of the lower intensities for the high-energy spin-orbit components for v^+=1-9 is consistent with the decay of the high-energy spin-orbit components by the field induced spin-orbit/rotational autoionization. The enhancements observed for the low-energy spin-orbit components for hydrogen halides resulting from this mechanism have been well documented.

C. Spectroscopic constants for $O_2^+(a^4P_{5/2,3/2,1/2,-1/2u}$, v^+=0-18) and $O_2^+(A^2P_u$, v^+=0-12)

Based on BOS simulation, we obtained accurate ionization energies, vibrational constants, rotational constants and spin-orbit splitting constants for both cases. Therefor vibrational(ω_e^+, $\omega_e^+x_e^+$, $\omega_e^+y_e^+$, and $\omega_e^+z_e^+$) and rotational (B_e^+, α_e^+, and γ_e^+) Dunham coefficients are derived accurately and agree with previous reports excellently.

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